

Structural Studies of Microcrystalline Porphyrins

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Beamline(s): X7B

Introduction: Porphyrins are tetrapyrrole derivatives that mediate a spectrum of bioenergetic reactions ranging from photosynthetic energy transduction to conversion of carbon dioxide into fuel. Their structures have been widely studied to ascertain the factors that control bioenergetic and catalytic reactions. In addition, porphyrins in which the macrocycle is oxidized, i.e. cation radicals, are important intermediates in the catalytic cycles of heme proteins and in photosynthetic processes [1]. In order to assess the stereochemical consequences of oxidation on the porphyrin skeleton, we are systematically examining the structures of porphyrin cation radicals and their neutral precursors, such as **1**, and subsequently mapping their electron density distributions. Changes in conformation that occur upon oxidation have been shown to alter the chemical and physical properties of porphyrin complexes and may dictate their reactivity in vivo [2]. Other recent applications of porphyrins whose structures we have pursued at X7B are as sensitizers for photodynamic therapy [3], in self-assembled arrays [4] with potential applications to materials chemistry as photonic devices, conductive polymers and molecular wires, and as models for enzymatic catalysis [5].

Methods and Materials: For each compound, at least two hemispheres of data were collected by the rotation method using a MAR345 image plate detector at liquid nitrogen temperature. The data were processed and merged with Denzo/Scalepack [6] and the structures were refined with the SHELXTL package [7].

Results: As part of our program to characterize known porphyrin radicals and their neutral precursors, we obtained a new polymorph of pyridine-Zn(II)octaethylporphyrin, shown in Figure 1.

Conclusions: The structures provide unambiguous identification of the compounds. In addition, they form the basis for calculations that serve to test theoretical treatments and to predict the properties of new porphyrins.

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Figure 1. Molecular structure of **1**, a new form of (pyridine)-Zn(II)octaethylporphyrin. The asymmetric unit consists of three distinct porphyrins that exhibit subtle differences in conformation (and thus make it an unattractive candidate for electron density studies).